

(19) Japanese Patent Office (JP)

(11) Unexamined Patent Application No:

**9-286758**

**(12) Unexamined Patent Gazette (A)**

(43) Date of Publication: 4 November 1997

(51) Int. Cl. <sup>6</sup>	Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
C07C 63/26		2115-4H	C07C 63/26	N
C07C 51/265		2115-4H	C07C 51/265	
C07C 51/43		2115-4H	C07C 51/43	
C07C 51/487		2115-4H	C07C 51/487	
Request for Examination: Not yet submitted		Number of Claims: 6 OL	Total of 7 pages [in original]	
(21) Application No.:	8-96979	<div>(71) Applicant: 000004466 Mitsubishi Gas Chemical Company, Inc. 5-2 Marunouchi 2-chome, Chiyoda-ku, Tokyo</div> <div>(71) Applicant: 000003160 Toyobo Co., Ltd. 2-8 Dojimahama 2-chome, Kita-ku Osaka City, Osaka</div> <div>(71) Applicant: 592162324 Mizushima Aroma Company, Ltd. 3-1 Mizushima Nakadori 2-chome, Kurashiki-shi Okayama Prefecture</div> <div>(72) Inventor: Fumiya ZAIMA c/o Mizushima Plant, Mitsubishi Gas Chemical Company, Inc., 10 Mizushima Kaigandori 3-chome Kurashiki-shi, Okayama Prefecture</div>		
(22) Date of Filing:	18 April 1996			
(Continued on last page)				

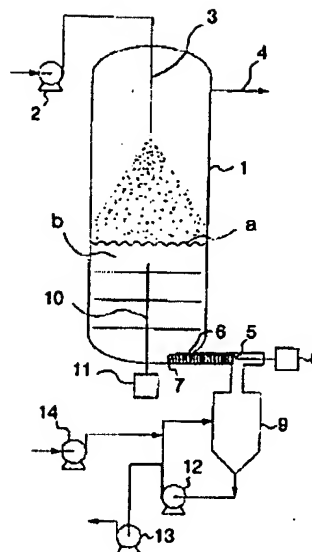
**(54) [Title of the Invention]**

**Method for Manufacturing High-Purity  
Terephthalic Acid**

**(57) [Summary]**

**[Object]** A method for manufacturing high-purity terephthalic acid wherein the mother liquor of an acetic acid solvent slurry of terephthalic acid crystals obtained by the liquid-phase oxidation of a *p*-alkylbenzene is replaced with a water solvent slurry and a catalytic hydrogenation treatment is subsequently performed, resulting in a shortening of the process flow, and accordingly a reduction in the capital investment and costs associated with the operation.

**[Means of Achievement]** An acetic acid solvent slurry is introduced to the upper region of a mother liquor replacement column, terephthalic acid crystals precipitate and accumulate in the lower region to form a terephthalic acid crystal layer, a quantity of replacement water sufficient to form a rising current of water in the interior of the column is supplied via the bottom of the column, and the layer of accumulated terephthalic acid crystals is extracted from the bottom of the column. Arm-type stirring blades are provided within the accumulated layer, and the fluidity of the accumulated layer is maintained by the gentle rotation of the stirring blades.



**[Claim(s)]**

**[Claim 1]** A method for manufacturing high-purity terephthalic acid wherein the mother liquor of an acetic acid solvent slurry of terephthalic acid crystals obtained by the liquid-phase oxidation of a *p*-alkylbenzene is replaced with a water solvent slurry, and a catalytic hydrogenation treatment is subsequently performed, wherein the method for manufacturing high-purity terephthalic acid is characterized in that the acetic acid solvent slurry is introduced to the upper region of a mother liquor replacement column, terephthalic acid crystals precipitate and accumulate in the lower region to form a terephthalic acid crystal layer, a quantity of replacement water sufficient to form a rising current of water in the interior of the column is supplied via the bottom of the column, and the layer of accumulated terephthalic acid crystals is extracted from the bottom of the column, with arm-type stirring blades being provided within the accumulated layer, and the fluidity of the accumulated layer being maintained by the gentle rotation of the stirring blades.

**[Claim 2]** The method for manufacturing high-purity terephthalic acid according to Claim 1, characterized in that the replacement water is supplied intermittently.

**[Claim 3]** The method for manufacturing high-purity terephthalic acid according to Claim 1 or 2, wherein the replacement water is supplied while being caused to pulsate.

**[Claim 4]** The method for manufacturing high-purity terephthalic acid according to Claim 1, wherein the pulsation is provided to the bottom region of the mother liquor replacement column.

**[Claim 5]** The method for manufacturing high-purity terephthalic acid according to Claim 1, wherein the arm-type stirring blades are made to rotate at 0.1 to 20 rpm.

**[Claim 6]** The method for manufacturing high-purity terephthalic acid according to Claim 1, wherein the replacement water that flows from the bottom region of the accumulated layer is supplied via the stirring blades provided in the accumulated layer.

#### **[Detailed Description of the Invention]**

**[0001]**

**[Technical Field of the Invention]** The present invention relates to a method for manufacturing high-purity terephthalic acid, and more specifically relates to a mother liquor replacement method wherein water is used to replace the mother liquor of an acetic acid solvent slurry of crude terephthalic acid crystals obtained by means of a liquid-phase oxidation reaction.

**[0002]**

**[Description of the Prior Art]** Terephthalic acid is manufactured by subjecting a *p*-phenylene compound such as a *p*-alkylbenzene, typically *p*-xylene, to a liquid-phase oxidation reaction, and when acetic acid is used as a solvent (mother liquor), it is common to use a catalyst comprising cobalt or manganese, or such a catalyst further compounded with a bromine compound, acetaldehyde, or other accelerator. Nevertheless, the reaction product will contain 4-carboxybenzaldehyde (4CBA), *p*-toluylic acid, and a variety of color-imparting impurities, which accordingly necessitates a highly advanced purification technique to be used in order to obtain high-purity terephthalic acid.

**[0003]** Methods known for purifying crude terephthalic acid obtained by liquid-phase oxidation include dissolving the crude terephthalic acid in a water solvent under high temperature and pressure, and performing a catalytic hydrogenation treatment, oxidation treatment, recrystallization treatment, high-temperature immersion treatment using a slurry containing partially dissolved terephthalic acid crystals, or other treatment. In particular, methods in which the crude terephthalic acid is dissolved in water and a Group VIII noble metal catalyst is used under high temperature and pressure to perform the catalytic hydrogenation treatment step have a decades-long history of use in large-scale industrial processes employed in the manufacture of high-purity terephthalic acid.

[0004] Nevertheless, a significant problem is created by the lengthy process flow required by methods in which a catalytic hydrogenation treatment step is performed. In other words, even if the complicated and troublesome units used for solvent recovery, catalyst recovery, and the like are omitted, the process flow in its main form will have an oxidation reactor having one or more stages, several consecutive crystallizers for the crude product, a separator for the crude product, a dryer for the crude product, a redissolving vessel, a catalytic hydrogenation reactor, several consecutive crystallizers for the refined product, a separator for the refined product, and a dryer for the refined product that are linked in series.

[0005] Major factors cited as contributing to the length of the process flow as described in the foregoing are the use of acetic acid as a reaction solvent when oxidation is employed in the manufacture of crude terephthalic acid, and the use of water as a reaction solvent when a catalytic hydrogenation treatment is used for purification purposes. In order to replace the acetic acid solvent with a water solvent, the crude terephthalic acid produced as a result of oxidation must be completely separated from the acetic acid solvent and then re-dissolved in the water solvent. If the crude terephthalic acid has not been completely separated from the acetic acid, and the crude terephthalic acid is fed to the catalytic hydrogenation treatment step with the acetic acid solvent adhering thereto, the acetic acid will be virtually unaltered in a chemical sense as a result of the catalytic hydrogenation treatment; therefore, the acetic acid solvent adhering to the crude terephthalic acid will contaminate the water solvent during the catalytic hydrogenation treatment, and will be discharged from the system. As a result, considerable economic losses will result because the costly acetic acid will be lost as effluent, and the acetic acid effluent will need to be rendered harmless to the environment.

[0006] In order to control such economic losses it is necessary to combine a dryer for the crude product with a separator for the crude product that is used to separate the mother liquor from the slurry that contains the crystals obtained in the oxidation step, so that the acetic acid will be almost entirely prevented from adhering to the crude terephthalic acid fed to the catalytic hydrogenation step. Flows incorporating such separator/dryer combinations are currently being used in industrial-scale equipment. The most common methods used for separating the mother liquor from the slurry containing the crystals involve centrifugal separators or rotary vacuum filters, both of which are extensively used when mother liquors are to be separated from slurries containing crystals of crude terephthalic acid.

[0007] With methods using centrifugal separators, a feedstock acetic acid slurry is introduced into a basket rotating at high speed, which causes the mother liquor to overflow from the upper region and the crystals to be directed to the lower region, but a drawback exists insofar as the structural requirements of centrifugal separators that rotate at high speeds entail complicated repairs and maintenance. Moreover, the crude terephthalic acid crystals cannot be rinsed in a simple manner, which means that the mother liquor cannot be completely removed.

Consequently, a drying step must be provided downstream from the centrifugal separation step in order to remove any remaining acetic acid that has adhered to the crude terephthalic acid.

[0008] With rotary vacuum filters, the crude terephthalic acid that has accumulated in the bottom region of the housing adheres to the filter element, and rises up and rotates in concert with the rotation of the filter element. After having been passed through a rinsing point, the crystals are typically separated in the form of a cake. This technique does not require rotation to be performed at high speeds, and therefore involves comparatively simple repair work and maintenance; however, the difficulties encountered with completely removing the mother liquor attached to the crude terephthalic acid crystals necessitate the use of a dryer downstream, as with centrifugal separators.

[0009] Methods for separating the crystals and removing the mother liquor that do not involve the use of centrifugal separators or rotary vacuum filters include the method cited in JP (Kokoku) 33-5410, wherein a slurry in which the crude terephthalic acid has been recrystallized with water is fed to an upright tube at a high temperature (165°C or higher), the terephthalic acid crystals precipitate against the gentle upward current as a result of gravity, and any mother liquor adhering thereto is washed away. In this method, the terephthalic acid crystals are recrystallized in a water solvent, after which the crystals and mother liquor are separated under high temperature (and under compression); however, this method is basically a mother liquor replacement method wherein the mother liquor of the terephthalic acid slurry is replaced with fresh solvent.

[0010] This mother liquor replacement method utilizes gravity to cause the crystals to precipitate; the method is accordingly exceptional because it obviates the use of any special motive force, while also being attractive due to the simplicity of the equipment required. Nevertheless, the method has drawbacks relating to a low mother liquor replacement rate and to the difficulties encountered when the method is directly scaled up based on the experimental

results. The rising current of high-temperature water may be increased in order to improve the mother liquor replacement rate, but this will necessitate the use of large volumes of solvent (water). Increasing the rising current will also reduce the crystal precipitation rate and will cause large quantities of crystals having small particle sizes to overflow from the top region of the upright tube.

[0011] The mother liquor replacement method proposed in JP (Kokai) 57-53431A is intended to resolve such drawbacks by using a combination of a particle conveying step and a step for causing terephthalic acid crystals to precipitate under gravity, divided by a plurality of transversely oriented perforated partitioning plates. These partitioning plates are used to prevent channeling and back-mixing of the fluids in the apparatus, and accordingly increase the mother liquor replacement rate; however, when mother liquor replacement is performed with a slurry being subjected to gravity-assisted precipitation, the presence of such partitioning plates leads to the accumulation of crystals thereon, clogging of the openings, and bulking, for which reasons labor-intensive efforts are required to achieve stable operation.

[0012] A mother liquor replacement column proposed in JP (Kokai) 1-160942A has a structure whereby multiple partitioning trays are provided in a transverse direction, and scraping blades that rotate relatively slowly above each tray scrape the terephthalic acid crystals off the trays. A high mother liquor replacement rate, which is estimated to be at least 99%, is achieved in the cited examples by using water to replace the acetic acid solvent (mother liquor) of the crude terephthalic acid using the aforesaid replacement column. The amount of feedstock terephthalic acid slurry is approximately one ton/hour in the laboratory-scale equipment used in the examples; however, on an industrial scale, approximately 100 times the amount of terephthalic acid slurry used in the examples needs to be treated, and the size of a mother liquor replacement column able to treat such quantities would presumably require a lateral cross-sectional area approximately 100 times as large as that of the replacement column cited in the examples. In other words, the rate at which the terephthalic acid crystals precipitate in the equipment is governed by the characteristics relating to gravity and the solvent; therefore, irrespective of the size of the column, the lateral cross-sectional area of the mother liquor replacement column must be increased approximately 100-fold under constant conditions, requiring the mother liquor replacement column to be of an enormous size in order for the high mother liquor replacement rate specified in the foregoing to be achieved.

[0013]

**[Problems That the Invention Is Intended to Solve]** If a mother liquor replacement column is used to substitute water for the mother liquor of the acetic acid solvent slurry of the crude terephthalic acid crystals obtained by liquid-phase oxidation, and the resulting water slurry of the crude terephthalic acid is introduced into a catalytic hydrogenation treatment apparatus, then it is possible to dispense with the separators and dryers used in current process flows to separate the mother liquor from the slurry obtained from the oxidation step. Nevertheless, there has yet to be perfected a serial industrial-scale mother liquor replacement method of the aforesaid description used to manufacture high-purity terephthalic acid; i.e., an actual technique able to assume the functions of the separators and dryers used in the process flows currently employed for the mother liquor of the crude terephthalic acid.

[0014] It is an object of the present invention to perfect a method in which water is used to replace the mother liquor of an acetic acid solvent slurry of crude terephthalic acid crystals obtained by liquid-phase oxidation, and the mother liquor of the resulting water slurry of crude terephthalic acid is directly fed to a catalytic hydrogenation treatment apparatus; and to achieve a shortening of the process flow in plants used to manufacture high-purity terephthalic acid, and, accordingly, a reduction in the capital investment and costs associated with the operation.

[0015] It is difficult to provide a strict delineation between the acetic acid loss and the economic loss caused by the attendant wastewater treatment load, because the boundary line must be established after having considered the various economic situations of the manufacturing plants. Nevertheless, the operation can be judged to be industrially feasible if the mother liquor replacement rate is generally 99% or higher. If the mother liquor replacement rate exceeds 99.9%, then the operation can be judged to be definitively feasible. It is accordingly a specific goal of the present invention to perfect a mother liquor replacement method that is more efficient than conventional mother liquor replacement methods, and is able to achieve a mother liquor replacement rate of 99% or higher, and preferably 99.9% or higher.

[0016]

**[Means Used to Solve the Above-Mentioned Problems]** The present inventors conducted years-long studies in order to surpass the technological concepts and advances made over the past several decades as well as the technical obstacles encountered during that time, and as a

result submitted a patent application (JP (Tokugan) 7-118299) based on having discovered that a mother liquor replacement rate of 99% or higher could be achieved through the use of a compact and simple apparatus by forming a layer of accumulated terephthalic acid crystals in the lower region of the mother liquor replacement column and feeding water via the bottom of the column. The present inventors performed further investigations, and arrived at the present invention as a result of having discovered that if stirring blades having a plurality of arms that extend in a horizontal direction were provided within the layer of accumulated terephthalic acid crystals (i.e., arm-type stirring blades) and gently caused to rotate; and if pulsation were provided by any relevant method to the layer of accumulated terephthalic acid, drift currents and channeling of the replacement water in the accumulated layer would be controlled, the dispersing of the replacement water would be improved, and the operability of the mother liquor replacement column could be dramatically improved as well.

[0017] In other words, the present invention is a method for manufacturing high-purity terephthalic acid wherein the mother liquor of an acetic acid solvent slurry of terephthalic acid crystals obtained by the liquid-phase oxidation of a *p*-alkylbenzene is replaced with a water solvent slurry, and a catalytic hydrogenation treatment is subsequently performed, wherein the method for manufacturing high-purity terephthalic acid is characterized in that the acetic acid solvent slurry is introduced to the upper region of a mother liquor replacement column, terephthalic acid crystals precipitate and accumulate in the lower region to form a terephthalic acid crystal layer, a quantity of replacement water sufficient to form a rising current of water in the interior of the column is supplied via the bottom of the column, and the layer of accumulated terephthalic acid crystals is extracted from the bottom of the column, with arm-type stirring blades being provided within the accumulated layer, and the fluidity of the accumulated layer being maintained by the gentle rotation of the stirring blades.

[0018]

**[Embodiments of the Invention]** The acetic acid solvent slurry of the crude terephthalic acid crystals whose mother liquor is to be replaced is typically manufactured by the oxidation of a *p*-phenylene compound such as a *p*-alkylbenzene, typically *p*-xylene, and it is common to use a catalyst comprising a salt of cobalt, manganese, or another heavy metal; or such a catalyst further compounded with an accelerator such as a bromine compound, acetaldehyde or the like. Acetic



acid having a water content of approximately 3 to 20% is used as the solvent. Atmospheric air or oxygen is ordinarily used as the molecular oxygen, and the reaction is typically performed in one or more stages at a temperature of 170 to 230°C and a pressure of 10 to 30 atm.

[0019] The slurried reaction effluent obtained from the liquid-phase oxidation step will contain 4CBA, *p*-toluyllic acid, catalysts, and a variety of other impurities along with the terephthalic acid crystals. The reaction effluent is introduced into a crude-type consecutive crystallizer over one or more stages, and the terephthalic acid that has dissolved in the solvent is recrystallized as the temperature is successively lowered to a prescribed level. The acetic acid solvent slurry of the terephthalic acid crystals is subsequently transferred to a mother liquor replacement column and introduced into a rising current of water therein, whereupon a small amount of terephthalic acid microcrystals in the oxidation reaction mother liquor flows upwards in concert with the rising water current, while the majority of the terephthalic acid crystals settle inside the column.

[0020] The terephthalic acid crystal precipitate is extracted from the column bottom in slurried form, but in the present invention a layer of accumulated precipitate is formed in the lower region of the column, and replacement water is supplied from within the accumulated layer. Adopting a method whereby the replacement water is fed sprinkler-like via arm-type stirring blades provided within the accumulated layer, or via a ring header provided within the accumulated layer, is also effective in improving the dispersing of the replacement water through the accumulated layer while preventing channeling and drift currents. The accumulated layer in the bottom region of the column is extracted via any known continuous or intermittent technical procedure. Individual terephthalic acid crystals in the accumulated layer will migrate downwards as a result. However, the presence of the rising current of water in the column will cause the terephthalic acid crystals and water to countercurrently contact one another, which will cause the acetic acid solvent remaining on the crystal surfaces to be washed off in a highly efficient manner together with the variety of byproducts contained in the acetic acid solvent as a result of the oxidation reaction. Because of this action, a water solvent slurry of the terephthalic acid crystals that contains essentially no acetic acid will be extracted from the column bottom. Without having to be subjected to any additional treatment, this water solvent slurry can be transferred to a step where high-purity terephthalic acid is manufactured by means of any of a variety of purification methods known in the art, and generally by dissolving the slurry under

high temperature and pressure and performing the catalytic hydrogenation treatment step in the presence of a Group VIII noble metal catalyst.

[0021] The essential conditions for implementing the present invention shall be outlined hereunder. A mother liquor replacement rate of 99% or higher, and preferably 99.9% or higher, must be achieved in the mother liquor replacement column, for which reason it is an essential condition that the fluidity of the layer of accumulated terephthalic acid crystals be maintained. It is also necessary to adopt an appropriate length (height) for the layer of accumulated terephthalic acid crystals and linear velocity (upward linear velocity) for the water flowing upwards through the column.

[0022] The length of the accumulated layer is determined according to a plurality of operating factors such as the rate at which the terephthalic acid slurry is fed from the upper region of the column, the rate at which the water is fed from the column bottom, and the rate at which the terephthalic acid slurry is extracted from the column bottom. This is achieved during actual operation by detecting the interface between the accumulated layer and the precipitation region in the mother liquor replacement column, and adjusting the rate at which the layer of accumulated terephthalic acid crystals is extracted so as to keep the interface in a prescribed position. A longer accumulated layer will result in a heightened washing effect and a higher mother liquor replacement rate, while a shorter layer will result in a diminished mother liquor replacement rate. The accumulated layer is therefore preferably made as long as possible, but blocking may occur as a result of the static pressure of the terephthalic acid crystals if the layer is too long; accordingly, the layer must not be unnecessarily long.

[0023] The mother liquor replacement rate is also indicated as a function of the diameter of the column, and in order to achieve a mother liquor replacement rate of 99% or higher, the length of the accumulated layer must be at least one-fifth the diameter of the mother liquor replacement column. The upward linear velocity expresses the volume of water flowing upwards as a countercurrent against the accumulated layer of terephthalic acid crystals, and for the sake of convenience is defined in terms of the empty column in the area of the accumulated layer. According to the collective experience of the present inventors, a higher upward linear velocity will result in an increased mother liquor replacement rate, but at velocities exceeding 3 m/h, the mother liquor replacement rate will generally drop sharply.

[0024] Consequently, when designing the mother liquor replacement column, the lower limit of the upward linear velocity should be set at a value greater than zero; i.e., a substantially rising current need only be formed, and the upper limit should typically be 3 m/h. Setting the upward linear velocity to a value in excess of the upper limit will not only reduce the replacement rate, but will result in some of the terephthalic acid crystals inadequately precipitating and being drawn upwards along with the rising liquid current. Water consumption will also increase as a result, which will elevate the concentration of water in the acetic acid mother liquor recovered from the top of the column.

[0025] There are no particular limitations as to the temperature of the mother liquor replacement column, but it is necessary to take a number of factors into account in relation to the entire apparatus used to manufacture the high-purity terephthalic acid. First, when mother liquor replacement is performed at higher temperatures, the resulting terephthalic acid will be of higher quality. In other words, when the product is obtained from the oxidation reactor and introduced to the crude-system consecutive crystallizer in ordinary terephthalic acid manufacturing equipment, a majority of the terephthalic acid produced as a result of the reaction will already be present in the form of crystals. By successively lowering the temperature in the crystallizer, the remainder of the terephthalic acid that has dissolved in the mother liquor will successively crystallize. It is a common phenomenon that crystals obtained in the high-temperature regions will be purer than those obtained at lower temperatures, but when terephthalic acid crystals are formed, 4CBA, which is present as an impurity, is known to form as a co-crystal together with the terephthalic acid, and will co-crystallize in dramatically higher proportions at lower temperatures. It is accordingly advantageous for mother liquor replacement to be performed at a high temperature, because the purity of the crude terephthalic acid in the resulting water slurry will improve, thereby enabling the high-purity terephthalic acid obtained via the catalytic hydrogenation treatment step to exhibit higher quality.

[0026] Second, the catalytic hydrogenation treatment reaction is performed at a high temperature; i.e., above 250°C, and if mother liquor replacement is performed at a relatively lower temperature, there will be an attendant loss of thermal energy. The oxidation reaction is normally performed at approximately 200°C; therefore, if mother liquor replacement is performed at a temperature that is significantly lower by comparison, the temperature will need to be repeatedly elevated and lowered, which will result in a loss of energy. Consequently,

mother liquor replacement<sup>1)</sup> is preferably performed at a temperature that is as close as possible to that at which the oxidation reaction is performed.

[0027] The mother liquor replacement column used in the present invention is an extremely simple apparatus having few power-driven components, and is accordingly simple to use at high temperatures and pressures. Nevertheless, at high temperatures, there will be an inevitable increase in the amount of terephthalic acid dissolved in the acetic acid solvent mother liquor that is discharged from the top of the mother liquor replacement column. This mother liquor is refluxed and reused as a solvent in the oxidation reaction; which does not directly contribute to a loss of terephthalic acid, but does cause a substantial decline in the reactor productivity. Taking these various conditions into account, the temperature in the mother liquor replacement step is preferably as much as 120°C lower than that of the oxidation reaction; i.e., approximately 80 to 180°C. The pressure in the mother liquor replacement column is one at which the temperature of the water and acetic acid can be maintained, and setting the temperature automatically sets the lower pressure limit; i.e., approximately 0 to 15 kg/cm<sup>2</sup>G.

[0028] As has been described in the foregoing, it is essential for the fluidity of the layer of accumulated terephthalic acid crystals to be preserved in the mother liquor replacement column. This stipulation is made because if the layer that has formed from the accumulation of terephthalic acid crystal precipitate is in a fully compacted state, its slurry characteristics will be compromised, and the layer will be impossible to extract from the bottom of the mother liquor replacement column using technical means. In order to prevent such an occurrence, the layer of accumulated terephthalic acid crystals must be fluidized at all times. Maintaining the fluidity of the accumulated layer will enable the dispersing of the replacement water feed to be promoted, and the replacement water to be prevented from forming a drift current and either channelling or rising through the layer of accumulated terephthalic acid crystals. If the accumulated layer becomes severely fluidized, the migration of substances therein will be accelerated, which will inevitably degrade the purification performance; i.e., the mother liquor replacement rate, of the mother liquor replacement column. It is essential to keep the fluidity of the accumulated layer to a very low level in order not to unreasonably lower the mother liquor replacement rate.

---

<sup>1)</sup> [Translator's note: The word "column" appears after "replacement", but has presumably been included erroneously, given the context.]

**[0029]** The most effective method for keeping the fluidity of the accumulated layer to a very low level is to use arm-type stirring blades. Another effective technique is to pulse the accumulated layer, using any method. Any arm-type stirring blade may be used provided that the arms extend horizontally away from the stirring shaft. Arms in the form of a straight line, cross, "comma," or other shape when viewed from above the stirring shaft may be used without any special restriction with regard to their number or shape. The number of arm stages is decided according to the height of the accumulated layer, and the cross-sectional profile of the arm may be round, triangular, rhomboid, or of any other configuration without special limitation as long as no significant motive force is required to shear the accumulated layer. The arm-type stirring blades preferably rotate at a rate of 0.1 to 20 rpm, and ideally at 0.5 to 10 rpm. The width of the arm-type stirring blades must be sufficient to cause the entirety of the layer of accumulated terephthalic acid crystals to flow. In an actual apparatus, the blade width is preferably 0.7 to 0.99 (and ideally 0.8 to 0.99) times the diameter of the mother liquor replacement column.

**[0030]** Methods for pulsing the accumulated layer include a method by which the replacement water is fed and halted in an alternately intermittent fashion; a method by which pulsing is performed by a pulsator installed on the replacement water supply line; and a method by which pulsing is performed by a pulsator mounted directly on the bottom region of the mother liquor replacement column; i.e., the region where the terephthalic acid crystal accumulates. If arm-type stirring blades of the above description are provided and are gently caused to rotate; and if pulsation is provided to the layer of accumulated terephthalic acid by means of any relevant method, drift currents and channeling of the replacement water in the accumulated layer will be controlled, the dispersing of the replacement water will be improved, and the operability of the mother liquor replacement column will be dramatically improved.

**[0031]**

**[Working Examples]** The present invention is described in detail below with reference to working examples; however, the present invention shall not be construed to be limited to these examples.

**[0032] Working Example 1**

The apparatus shown in FIG. 1 was used to perform experiments in which water was used to replace the mother liquor of a feedstock slurry obtained by liquid-phase oxidation, which was

an acetic acid solvent slurry of crude terephthalic acid crystals. The mother liquor replacement column 1 in FIG. 1 is a stainless steel container. A feedstock slurry introduction pipe 3 is provided to the upper region of the mother liquor replacement column and coupled to a feedstock slurry supply pump 2. A mother liquor discharging pipe 4 is provided to the top region of the column. The structure of the bottom region of the mother liquor replacement column is in the form of a semielliptical plate, to which is coupled a slurry tank 9. Refluxing and stirring are performed in the slurry tank 9 by means of a recirculating pump 12 that is mounted externally thereto. A branched pipe heading to a slurry extraction pump 13 and a branched pipe heading from a water supply pump 14 are coupled midway along the return pipe leading from the recirculating pump 12.

[0033] A screw conveyor guide pipe 6 is inserted into and connected to the column bottom, with an accumulated layer extraction port 7 formed therein as an opening that is cut off in an upwardly-facing, slantwise fashion. A screw conveyor 5 is disposed within the interior of the screw conveyor guide pipe 6, with one end of which extending to the accumulated layer extraction port 7 and the other end of which extending to the upper region of the slurry tank 9. The screw conveyor 5 is coupled to a motor 8 mounted externally thereto. The rippled line *a* shown in the transverse direction across the central region of the mother liquor replacement column 1 is the top surface of the layer of accumulated terephthalic acid crystals, with the height (length) of the accumulated layer being the distance from the rippled line *a* to the upper edge of the screw conveyor guide pipe 6.

[0034] With reference being made to FIG. 1, first, 100°C water was drawn into the system by driving the water supply pump 14. Once the water had started to overflow from the mother liquor discharging pipe 4, the recirculating pump 12 and slurry extraction pump 13 were activated. A motor 11 was also activated to turn arm-type stirring blades 10 at a rate of four rotations per minute. The feedstock slurry supply pump 2 was then activated, and a 150°C feedstock slurry was conveyed via the feedstock slurry introduction pipe 3. An acetic acid solvent slurry of terephthalic acid manufactured on an industrial scale was used as the feedstock slurry. The feedstock slurry was a reaction product obtained by oxidizing *p*-xylene at 195°C in a water-containing acetic acid solvent with air being blown thereinto in the presence of an oxidation reaction catalyst comprising a cobalt, manganese, and bromine compound. The reaction product was passed through a crystallizer in which the temperature was successively lowered over

several stages to yield a slurry cooled to 150°C, and the resulting slurry was transferred to the mother liquor replacement column 1. When the height of the accumulated layer reached a prescribed position while monitored with a powder surface detector, the motor 8 was activated, which caused the screw conveyor 5 to rotate, and crystal extraction to commence. Once the system had returned to a normal state, the respective flow rates were adjusted and set as described hereunder.

Feedstock slurry supply pump 2	783 kg/h (crystal concentration: 32.4%)
Slurry extraction pump 13	762 kg/h (crystal concentration: 33.3%)
Water supply pump 14	586 kg/h

[0036] Samples were collected from various locations on the apparatus after three days of continuous operation, and the compositions thereof analyzed. The results are displayed hereunder.

- (1) Mother liquor of feedstock slurry (supernatant obtained by cooling the sample collected from the feedstock slurry supply pump 2 to room temperature, and allowing the cooled slurry to stand)

Acetic acid	85.2%
Water	14.5%
Unidentified substances	0.3%

- (2) Extraction slurry (supernatant obtained from cooling the sample collected from the slurry extraction pump 13 to room temperature, and allowing the cooled slurry to stand)

Acetic acid	0.102%
-------------	--------

A mother liquor replacement rate based on acetic acid was 99.9% as calculated from the above result.

#### [0037] Comparative Example 1

The operation was performed in the same manner as described in Working Example 1 with the exception that the rotation of the arm-type stirring blades was halted. As a result, the accumulated layer lost fluidity, channelling occurred in the rising current of the replacement

water, bulking occurred in the bottom region of the column, the crystals could not be stably extracted from the bottom region of the column, and operation proved impossible.

**[0038]**

**[Effect of the Invention]** The method for manufacturing high-purity terephthalic acid of the present invention enables an extremely high mother liquor replacement rate to be obtained and the operability of a mother liquor replacement apparatus to be dramatically improved by causing arm-type stirring blades provided within the accumulated layer to gently rotate and thereby maintain the fluidity of the accumulated layer. This mother liquor replacement method dispenses with mother liquor separators and dryers used on crude terephthalic acid obtained as a result of liquid-phase oxidation reactions. The mother liquor replacement column is a compact and simple apparatus that readily enables an industrial-scale apparatus to be derived from a laboratory-scale one. The mother liquor replacement column is simple to operate under high temperatures and pressures, which enables high-purity terephthalic acid to be obtained in even higher levels of quality, and the number of crude terephthalic acid crystallizers to be reduced.

**[0039]** It is accordingly possible to shorten the process flow, which has been a major problem with conventional methods for manufacturing high-purity terephthalic acid, and to significantly reduce construction expenses while facilitating the operational procedure involved in manufacturing high-purity terephthalic acid. The method for manufacturing high-purity terephthalic acid of the present invention enables the costs incurred in servicing crude terephthalic acid mother liquor separators and dryers to be minimized, and an extremely high mother liquor replacement rate to be achieved; therefore, the amount of acetic acid solvent effluent produced by the liquid-phase oxidation reaction can be minimized, and any increase in the wastewater treatment load virtually eliminated. Consequently, the present invention enables the manufacture of high-purity terephthalic acid, which has tremendous industrial advantages.

#### **[Brief Description of the Drawings]**

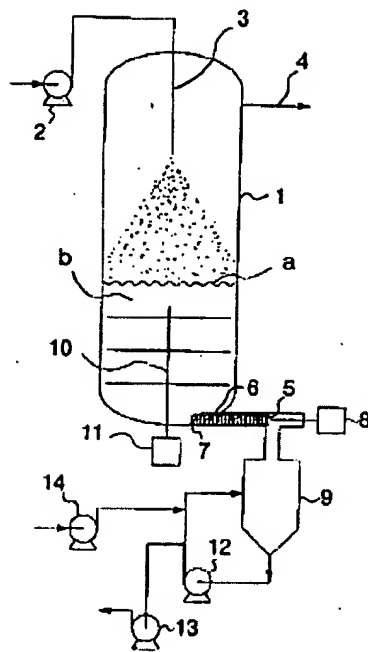
**[Figure 1]** Schematic diagram illustrating a mother liquor replacement apparatus employed in the examples



**[Key]**

1	mother liquor replacement column
2	feedstock slurry supply pump
3	feedstock slurry introduction pipe
4	mother liquor discharging pipe
5	screw conveyor used for crystal extraction
6	screw conveyor guide pipe
7	accumulated layer extraction port 7
8	motor
9	slurry tank
10	arm-type stirring blades
11	motor
12	recirculating pump
13	slurry extraction pump
14	water supply pump
<i>a</i> (rippled line)	top surface of accumulated layer
<i>b</i>	layer of accumulated terephthalic acid crystals

[Figure 1]



Continued from front page

---

(72) Inventor: Fumio OKOSHI  
c/o Mizushima Plant, Mitsubishi Gas  
Chemical Company, Inc., 10 Mizushima  
Kaigandori 3-chome, Kurashiki-shi,  
Okayama Prefecture

---

(72) Inventor: Masato INARI  
c/o Mizushima Plant, Mitsubishi Gas  
Chemical Company, Inc., 10 Mizushima  
Kaigandori 3-chome, Kurashiki-shi,  
Okayama Prefecture